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Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Trace Elements in Streambed Sediment and Fish Livers, 1995-96

By Sharon E. Kroening, James D. Fallon, and Kathy E. Lee

Water-Resources Investigations Report 00-4031

National Water-Quality Assessment Program

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Foreword

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policy makers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Chief Hydrologist

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Conversion Factors, Abbreviated Water-Quality Units, and Vertical Datum,

Multiply inch-pound unit	By	To obtain metric unit
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
ounce avoirdupois	28.35	gram
square mile (mi^2)	259.0	hectare
degrees Fahrenheit (°F)	°C = (°F - 32)/1.8	degrees Celsius (°C)

Concentrations of substances in sediments and fish are given in weight percent, or micrograms per gram (µg/g). A microgram is a millionth of a gram.

Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Trace Elements in Streambed Sediment and Fish Livers, 1995–96

by **Sharon E. Kroening, James D. Fallon, and Kathy E. Lee**

ABSTRACT

Trace elements were analyzed in streambed sediment and fish livers in part of the Upper Mississippi River Basin as part of the U.S. Geological Survey's National Water-Quality Assessment Program. The purpose of this report was to describe the occurrence and distribution of trace elements, describe the relations of concentrations measured to natural and anthropogenic factors, and describe any relation between concentrations in streambed sediment and fish livers. The study unit included the part of the Upper Mississippi River Basin from the river's source in northern Minnesota to the outlet of Lake Pepin, a natural lake on the river located near Red Wing, Minnesota. Streambed sediment samples were collected from 27 sites located throughout the study unit, and fish were obtained from 25 sites.

The occurrence and distribution of trace elements in streambed sediment were related to land use and the composition of surficial glacial deposits covering the study unit. Concentrations of antimony, arsenic, cadmium, copper, lead, mercury, nickel, and zinc in streambed sediment were primarily related to urban land use. Concentrations of these elements generally were greatest in streambed sediment collected at sites within or near urban areas in the study unit. The greatest concentrations of most of these elements were measured in streambed sediment obtained from Shingle Creek. Lead concentrations in streambed sediment Shingle Creek increased in the downstream direction. This pattern probably reflects the past use of leaded gasoline, pesticides, or paints.

Cadmium concentrations in sediment from the Mississippi River were greatest at Nininger, Minnesota and in Lake Pepin. This pattern suggested that inputs of cadmium into the river were from the TCMA.

Arsenic concentrations were greatest in streambed sediment collected from Cedar Creek, Shingle Creek, and the Vermillion River. Increased arsenic and iron concentrations in sediment from Cedar Creek, the Vermillion River, and the most upstream site on Shingle Creek suggested a local source of sulfide minerals or preferential sorption of arsenic to streambed sediment. The greatest concentrations of mercury were measured in streambed sediment collected from the Mississippi River at Grand Rapids and Minneapolis, Minnesota; Shingle Creek at 46th Street in Minneapolis, Minnesota; the Namekagon River above Spring Lake Creek near Hayward, Wisconsin; the St. Croix River at Hudson, Wisconsin; and the Vermillion River near Empire, Minnesota.

In fish livers, all of the trace elements analyzed were detected except antimony, beryllium, cobalt, and uranium. Trace element concentrations in fish livers generally did not show any pronounced patterns. Ranges for concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc were similar to those measured in 20 other NAWQA studies across the United States. Cadmium concentrations in fish livers were moderately correlated to fish length and weight. There were no relations between trace element concentrations in fish livers and streambed sediment.

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began full implementation of the National Water-Quality Assessment (NAWQA) Program. Long-term goals of the NAWQA Program are to describe the status of, and trends in, the quality of the Nation's freshwater streams, rivers, and aquifers and to identify the major natural and anthropogenic factors that affect the quality of these resources. Information from the NAWQA Program supports development and evaluation of management, regulatory, and monitoring decisions by other Federal, state, and local agencies that protect, use, and enhance water resources. Goals of the NAWQA Program are achieved through investigations of the Nation's most important river basins and aquifer systems, which are referred to as study units. Study units comprise diverse hydrologic systems of river basins, aquifer systems, or both, and are assessed on a nine-year cycle. More than two-thirds of the Nation's freshwater use occurs within the study units, and more than two-thirds of the people served by public water-supply systems live within these boundaries.

The Upper Mississippi River Basin (UMIS) study unit (fig. 1) encompasses an area of about 47,000 mi^2 primarily in the states of Minnesota and Wisconsin. The study unit includes the part of the Mississippi River from its source in northern Minnesota to the outlet of Lake Pepin, a natural lake on the river located near Red Wing, Minnesota. Land cover in the study unit is diverse and includes areas of agricultural lands, coniferous and deciduous forests, wetlands, lakes, and the seven-county Twin Cities (Minneapolis and St. Paul) metropolitan area (TCMA).

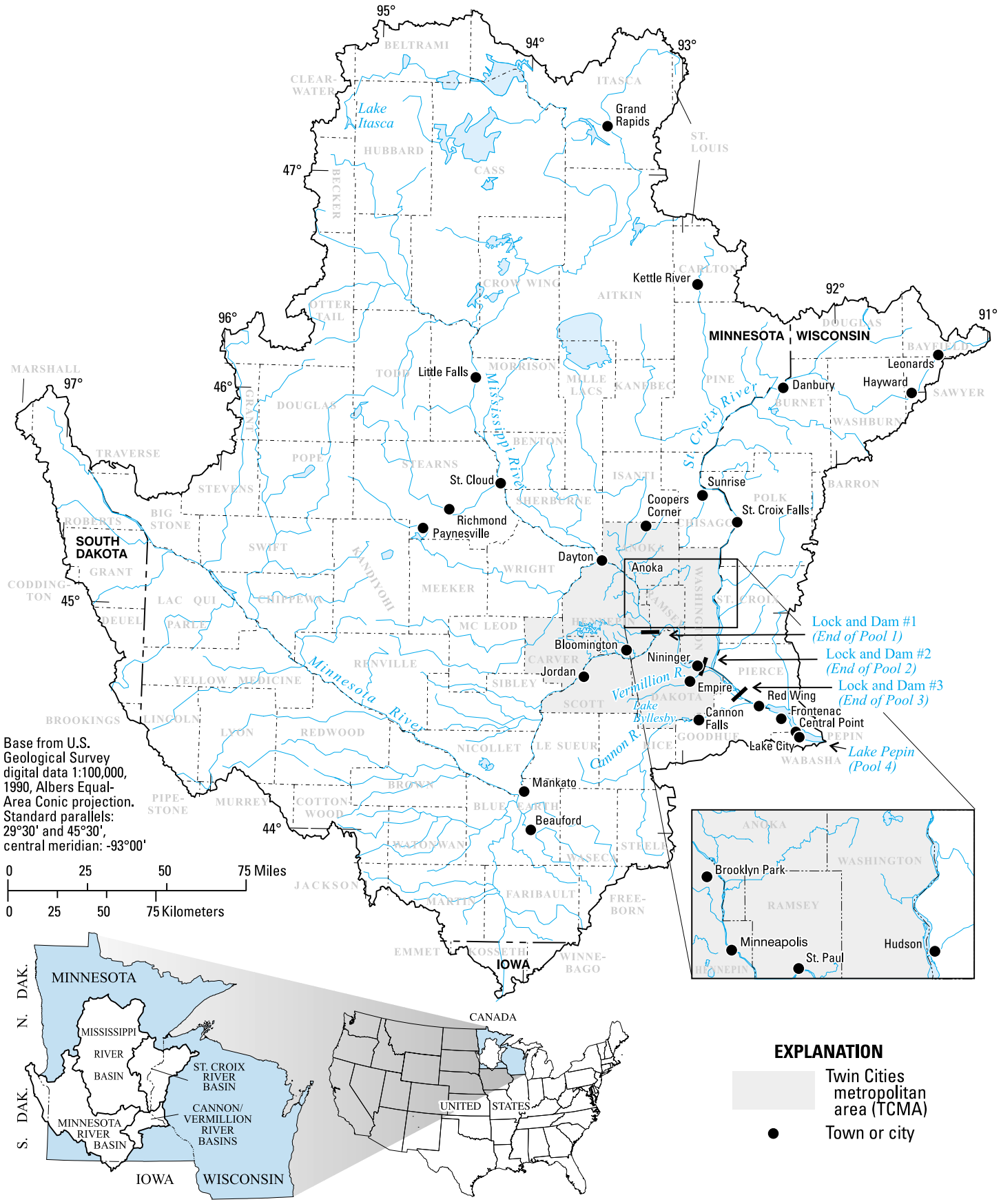

Figure 1.--Location of the Upper Mississippi River Basin study unit, Twin Cities metropolitan area, major rivers and streams, and selected towns and cities.

Concentrations of trace elements in streams and fish may vary as a result of natural and anthropogenic factors. Trace elements are present naturally as part of rocks, glacial deposits, and soils. The concentrations of trace elements in rocks vary depending upon the types of minerals present. For example, arsenic may be present naturally in sulfide minerals such as pyrite (Bhumbla and Keefer, 1994). Pyrite is known to be present in Cretaceous-age shales in the study unit, so a natural source of arsenic is possible in areas of shale outcrops. In addition, much of the study area is covered by glacial material deposited by ice and meltwaters during the last episode of Pleistocene glaciation. The source of much of this material is far to the north, northeast, and northwest of the study unit and is not local bedrock. These deposits, composed primarily of disaggregated bedrock, present a major redistribution of trace elements within the surficial environment. Thus, the natural distribution of trace elements in the study unit is, in part, controlled by the source bedrock type, mineral type, and glacial history.

Anthropogenic activities have altered the distribution of trace elements in the environment. The burning of fossil fuels and smelting of metals have increased emissions of trace elements to the atmosphere. Trace elements are present in materials used for a variety of purposes, which include electroplated coatings, flame retardants, gasoline additives, paints, pigments, pesticides, storage batteries, and wood preservatives (Fergusson, 1990). Trace elements may reach streams from these sources by atmospheric deposition, direct discharges, or as a result of erosion and transport of contaminated soils.

The chemical properties of sediment also may affect the ability of the sediment to retain trace elements. Iron and manganese oxides, organic matter, and clay minerals are able to variably retain or release a number of trace elements in differing chemical environments (Horowitz, 1991).

Some trace elements such as cobalt, copper, iron, manganese, molybdenum, and zinc are essential micronutrients for life (Gough and others, 1979). However, at increased concentrations, these and other trace elements such as arsenic, cadmium, chromium, lead, mercury, and selenium can be toxic to humans, plants, and animals. Within the study unit, people are recommended by the Minnesota Department of Health (1996) and the Wisconsin Department of Natural Resources (1994) not to eat, or to limit the consumption of, fish in certain streams because of increased mercury concentrations in fish tissues.

As part of the NAWQA Program, trace elements are assessed in streambed sediment and aquatic biota. Trace element concentrations in streambed sediment and aquatic biota generally are much greater than those typically found in water and are more likely to be detected with current analytical methods in these media. Concentrations of dissolved trace elements in water generally are low because of the strong affinity many of these elements have for the metal oxides and organic matter that comprise sediment (Horowitz, 1991; Hart, 1982). Trace elements also may be more concentrated in aquatic biota than in water because of bioconcentration, bioaccumulation, or biomagnification (Crawford and Luoma, 1993).

Purpose and Scope

The purpose of this report is to (1) describe the occurrence and distribution of trace elements in streambed sediment and fish livers in part of the UMIS study unit, (2) describe relations of trace element concentrations in streambed sediment and fish livers to natural and anthropogenic factors, and (3) describe any relation between trace element concentrations in streambed sediment and fish livers. The data evaluated were collected during 1995 and 1996 as part of an occurrence and distribution survey of trace elements in streambed sediment and aquatic biota for the UMIS study unit.

Environmental Setting of the Study Unit

The underlying bedrock in the study unit is a complex system of igneous, metamorphic, and sedimentary rocks, Precambrian to Cretaceous in age. In the northeastern part of the study unit, the bedrock is Precambrian red sandstone and basalts (Green, 1982). These rocks are known to contain minor copper and copper-iron sulfide minerals (Nicholson and others, 1992). The bedrock in the northern and southwestern parts of the study unit is principally Precambrian granites and gneisses (Ojakangas and Matsch, 1982) overlain by Cretaceous sandstones and shales (Wright, 1972). In the southeastern part of the study unit, the bedrock consists of Paleozoic sandstones and carbonates overlying Precambrian rocks.

Bedrock outcrops generally are sparse in the study unit, except in some river valleys. For the most part, the present landscape of the study unit was shaped during the Pleistocene Epoch, when the Laurentide Ice Sheet covered much of the region. Glaciation during this epoch occurred as a series of multiple ice advances and retreats which left layers of glacial deposits covering the study unit (fig. 2), ranging in thickness from zero to more than 600 feet thick. The Superior and Rainy Lobes advanced through the northern or northeastern parts of the study unit: whereas, the Des Moines and Wadena Lobes advanced from central Canada into the northwestern and western parts of the study unit. Because the Rainy and Superior Lobes primarily advanced over basalts and sandstones, glacial deposits from these ice sheets are principally siliceous. In contrast, the Des Moines and Wadena Lobe deposits contain Paleozoic limestone and dolomite from southern Manitoba and are much more calcareous in composition than deposits from the Superior or Rainy Lobes. As a result of differing parent materials, glacial deposits in the study unit may be classified by their mineral composition. This classification is complicated in some areas of the study unit, such as just north of the TCMA. In these areas, the Des Moines and Superior Lobes both traversed the same location at different times (Ojakangas and Matsch, 1982), so calcareous and siliceous glacial deposits are interbedded.

Glacial deposits covering the study unit also can be classified by how they were deposited. Unstratified deposits primarily consist of till plains and moraines, which generally are an unsorted mixture of clay, silt, sand, and gravel deposited directly from the ice, either beneath the ice sheet or at the margin; these deposits

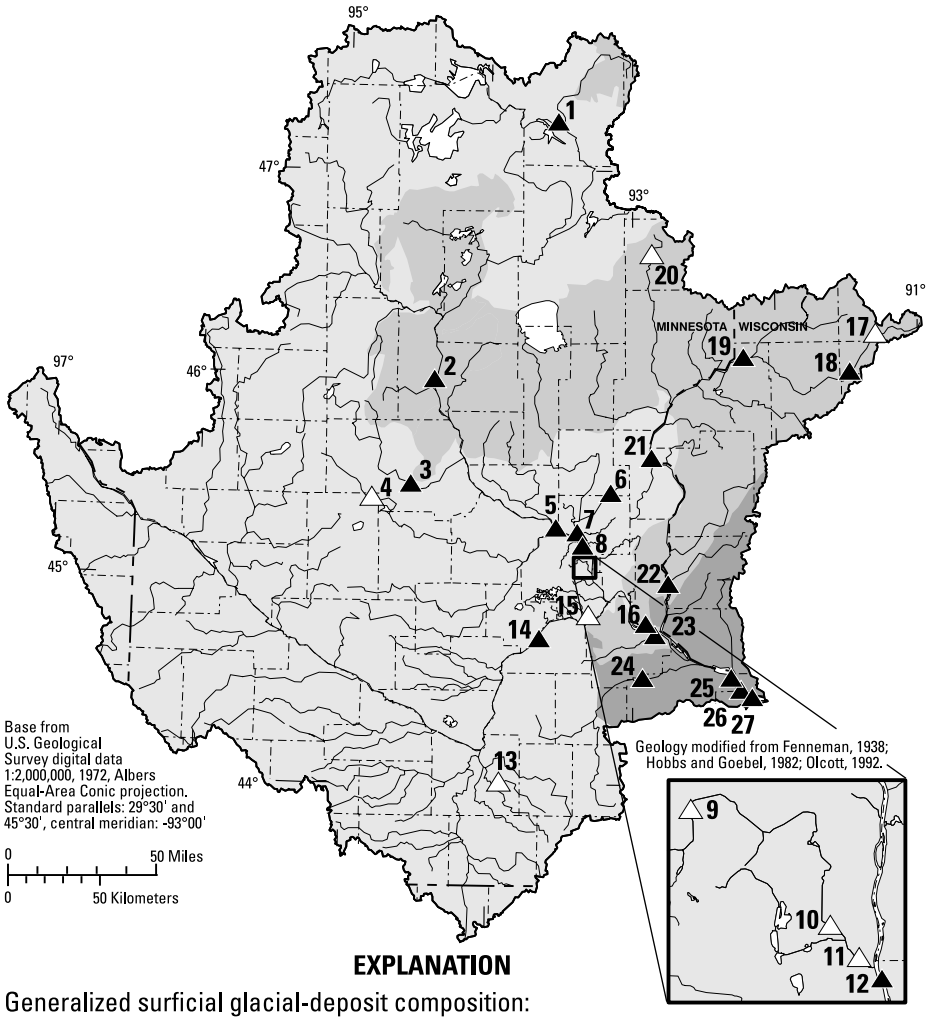

Figure 2.--Generalized glacial-deposit composition and location of streambed sediment and fish liver sampling sites in the Upper Mississippi River Basin study unit.

area hereinafter referred to as unsorted. Stratified deposits consist of alluvial deposits or outwash material, which is sorted sand and gravel deposited from meltwater flowing on top of, along the margin of, or in front of the ice; these deposits are hereinafter referred to as sorted.

The topography of the study unit consists of gently rolling hills, plains, and a multitude of lakes. There are two physiographic provinces within the study unit—the Superior Upland in the northeast and the Central Lowland in the south and west (Fenneman, 1938). The Superior Upland, which occupies the northeastern part of the study unit, is characterized by flat to hilly moraines and outwash plains. The Central Lowland Province is further categorized into the Western Lake, Wisconsin Driftless and Dissected Till Plains Sections. The Western Lake Section occupies most of the Central Lowland Province within the study unit. The land surface of this section was formed during the last episode of glaciation during the Pleistocene and is characterized by flat to rolling ground moraines, outwash plains, and glacial lake plains. The Wisconsin Driftless and Dissected Till Plains Sections occupy the southeastern part of the study unit and are characterized by more hilly terrain (Stark and others, 1996).

From its origin in northern Minnesota to Lake Pepin, the Mississippi River is fed by many small rivers and streams, as well as two major rivers: the Minnesota and St. Croix (fig. 1). Streamflow in these rivers varies seasonally. An analysis of data at selected USGS gaging stations by Stark and others (1996) showed that streamflows in the study unit generally are greatest in the spring and early summer as a result of melting snow, rains falling on melting snow, or heavy rains falling on saturated soils.

Land use and land cover across the study unit can be characterized by three zones: an agricultural zone across the southwestern one-third of the study unit; a forested zone across the northeastern one-third of the study unit; and a transitional zone in between (fig. 3). Urban land use comprises two percent of the study unit. The majority of the urban land (nearly 80 percent) in the study unit is concentrated in the TCMA. Other urban communities in the study unit include St. Cloud, Mankato, and Grand Rapids.

Acknowledgments

The authors gratefully acknowledge the National Park Service for sampling the site on the Namekagon River above Spring Lake Creek near Hayward, Wisconsin.

APPROACH

Sampling Design

A detailed description of the design of this trace element study is given by Stark and others (1999). A total of 27 sites were sampled (figs. 2 and 3; table 1). Sites were selected to (1) characterize the occurrence and distribution of trace elements in the major rivers within the study unit, and (2) assess the natural and anthropogenic fac-

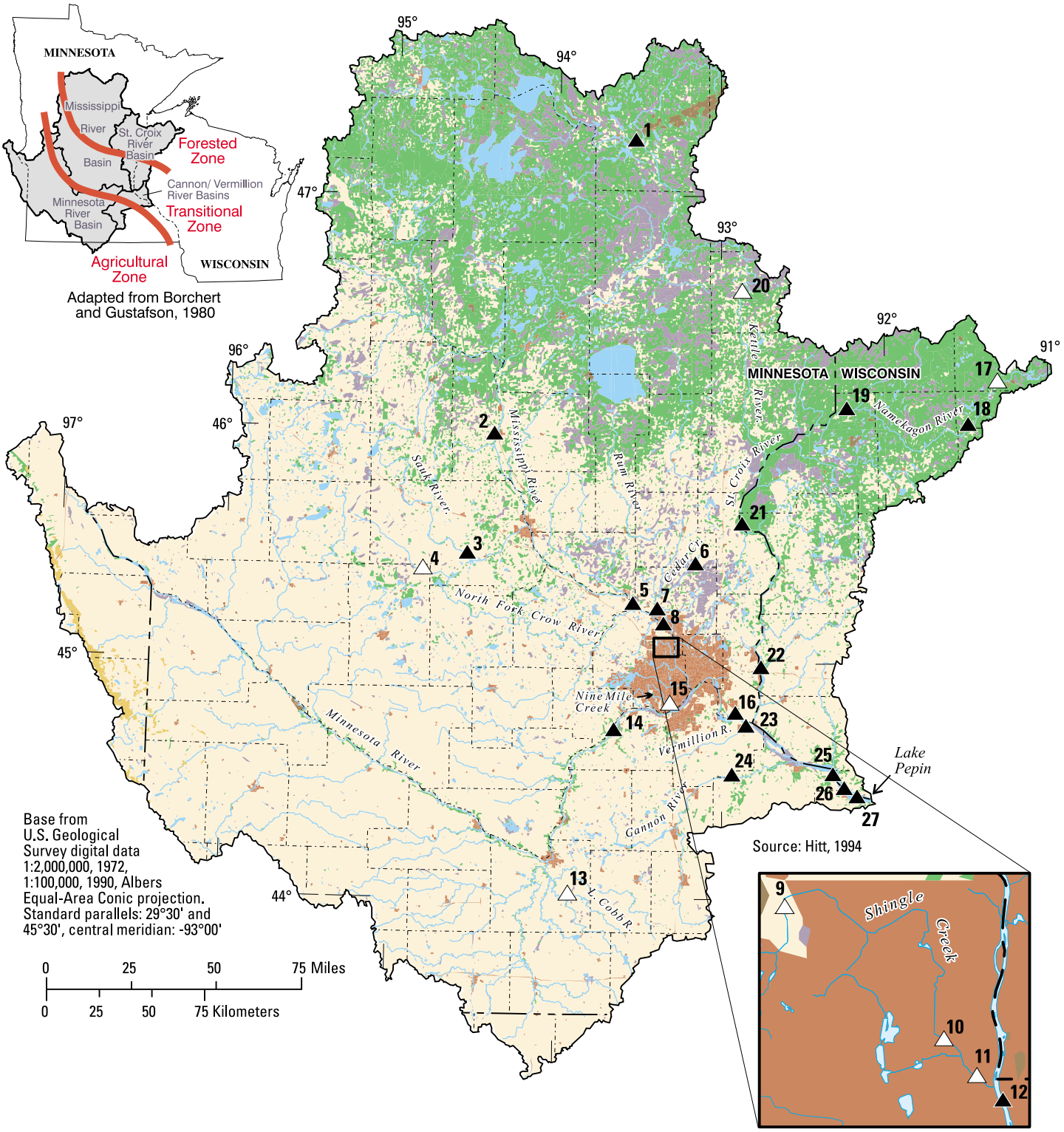

Figure 3.--Hydrography and land use and land cover in the Upper Mississippi River Basin study unit.

Table 1. Sites at which streambed sediment and fish livers were sampled in the Upper Mississippi River Basin study unit, 1995-96

[Sites are listed in downstream order; USGS, U.S. Geological Survey; ns, not sampled; mi^2, square miles; land use may not add to 100 percent due to rounding]

Map identifier (figures 2 and 3)	USGS site identifier	Site name	Latitude	Longitude	Sampling date		Dominant surficial geology	Dominant glacial deposit composition	Land use (percent)				Drainage area (mi^2)
					Sediment	Fish			Urban	Agricul-ture	Forest	Other	
1	05211000	Mississippi River at Grand Rapids, Minn.	47°13'56"	93°31'48"	7/25/95	7/24/95	Till plain-moraine	Calcareous	0.4	8.8	60	30.8	3,320
2	05263500	Mississippi River below Little Falls, Minn.	45°56'22"	94°23'20"	7/24/95	7/20/95	Till plain-moraine	Calcareous	0.6	24	49	25.6	11,300
3	05270380	Sauk River at Richmond, Minn.	45°26'56"	94°31'30"	7/20/95	7/19/95	Till plain-moraine	Calcareous	0.9	84	8.1	7.3	818
4	05276005	North Fork Crow River above Paynesville, Minn.	45°22'38"	94°47'00"	7/17/95 9/19/96	9/16/96	Outwash-alluvium	Calcareous	0.3	90	2.1	7.4	232
5	05280400	Crow River below State High-way 101 at Dayton, Minn.	45°13'20"	93°31'12"	7/24/95	7/18/95	Till plain-moraine	Calcareous	1.4	87	3.8	7.9	2,770
6	05286290	Cedar Creek near Coopers Corner, Minn.	45°23'31"	93°12'44"	9/16/96	10/4/96	Outwash-alluvium	Calcareous	0.1	69	7.8	23	27.3
7	05287000	Rum River at Anoka, Minn.	45°12'41"	93°23'11"	7/21/95	7/21/95	Till plain-moraine	Calcareous	0.7	49	21	29.6	1,560
8	05288500	Mississippi River near Anoka, Minn.	45°07'36"	93°17'48"	7/13/95	7/18/95	Outwash-alluvium	Calcareous	1.1	45	34	20.3	19,200
9	05288695	Shingle Creek at Zane Ave. at Brooklyn Park, Minn.	45°05'32"	93°21'22"	9/27/96	9/19/96	Outwash-alluvium	Calcareous	57	30	1.3	12	19.2
10	05288705	Shingle Creek at Queen Ave. in Minneapolis, Minn.	45°03'00"	93°18'36"	9/26/96	9/17/96	Outwash-alluvium	Calcareous	71	20	0.9	8.2	28.2
11	05288710	Shingle Creek at 46th Street in Minneapolis, Minn.	45°02'17"	93°17'30"	7/18/95	8/28/95	Outwash-alluvium	Calcareous	79	14	0.6	6.8	40.8
12	05288730	Mississippi River at 28th Ave. NE in Minneapolis, Minn.	45°01'12"	93°16'31"	9/27/96	11/11/96	Till plain-moraine	Calcareous	1.7	44	33	20.3	19,600
13	05320270	Little Cobb River near Beau-ford, Minn.	43°59'48"	93°54'30"	8/2/95 9/18/96	7/9/97	Till plain-Moraine	Calcareous	0.2	94	0.5	4.6	130
14	05330000	Minnesota River near Jordan, Minn.	44°41'35"	93°38'30"	7/11/95	7/10/95	Till plain-Moraine	Calcareous	0.9	94	1.7	3.5	16,200
15	05330902	Nine Mile Creek near James Circle at Bloomington, Minn.	44°48'26"	93°18'05"	7/18/95	7/26/95	Till plain-Moraine	Calcareous	87	5.7	2.2	5.4	44.6
16	05331570	Mississippi River at Nininger, Minn.	44°46'22"	92°54'07"	7/12/95	7/11/95	Till plain-Moraine	Calcareous	2.5	66	19	12.7	37,000
17	05331833	Namekagon River at Leonards, Wis.	46°10'18"	91°19'50"	7/19/95	7/25/95	Outwash-alluvium	Siliceous	0.7	1.8	78	19.3	128

Table 1. Sites at which streambed sediment and fish livers were sampled in the Upper Mississippi River Basin study unit, 1995-96(Continued)

[Sites are listed in downstream order; USGS, U.S. Geological Survey; ns, not sampled; mi^2, square miles; land use may not add to 100 percent due to rounding]

Map identifier (figures 2 and 3)	USGS site identifier	Site name	Latitude	Longitude	Sampling date		Dominant surficial geology	Dominant glacial deposit composition	Land use (percent)				Drainage area (mi^2)
					Sediment	Fish			Urban	Agricul-ture	Forest	Other	
18	05331873	Namekagon River above Spring Lake Creek near Hay-ward, Wisc.	45°59'22"	91°30'33"	9/17/96	10/26/96	Outwash-alluvium	Siliceous	1.4	5.5	78	15	208
19	05333500	St. Croix River near Danbury, Wisc.	46°04'28"	92°14'50"	7/19/95	9/27/95	Outwash-alluvium	Siliceous	0.3	4.9	79	16.3	1,510
20	05336180	Kettle River near Kettle River, Minn.	46°29'03"	92°53'19"	8/1/95	9/27/95	Till plain-moraine	Siliceous	0.0	23.4	43.4	33.2	157.2
21	05339770	St. Croix River near Sunrise, Minn.	45°34'14"	92°52'30"	7/20/95	7/14/95	Outwash-alluvium	Siliceous	0.4	24	59	18	5,510
22	05341552	St. Croix River at Hudson, Wisc.	44°58'57"	92°46'07"	7/14/95	7/14/95	Till plain-moraine	Siliceous	0.7	34	49	16.4	7,340
23	05345000	Vermillion River near Empire, Minn.	44°40'00"	93°03'17"	7/18/95	7/12/95	Outwash-alluvium	Calcareous	16	76	3.9	3.4	129
24	05355090	Cannon River at Lake Byllesby near Cannon Falls, Minn.	44°30'35"	92°57'00"	7/21/95	7/17/95	Till plain-moraine	Calcareous	3.1	89	2.6	5.6	1,150
25	443334092205201	Mississippi River at Lake Pepin near Frontenac, Minn.	44°33'34"	92°20'52"	7/28/95	ns	Till plain-moraine	Calcareous	2.3	62	22	12.9	47,300
26	442912092174201	Mississippi River at Lake Pepin at Central Point, Minn.	44°29'12"	92°17'42"	7/28/95	7/13/95	Till plain-moraine	Calcareous	2.3	62	22	12.9	47,300
27	442633092130801	Mississippi River at Lake Pepin near Lake City, Minn.	44°26'33"	92°13'08"	7/28/95	ns	Till plain-moraine	Calcareous	2.3	62	22	12.9	47,300

tors that affect trace element concentrations. Sites used for the first purpose are termed integrator sites because they represent large watersheds with multiple land uses. Sites used for the second purpose are termed indicator sites because they represent homogenous and specific land uses.

Eight sites were sampled on the Mississippi River and 3 sites were sampled on the St. Croix River to examine the longitudinal distributions of trace elements in those rivers (fig. 3, table 1). Streambed sediment were sampled at three sites in Lake Pepin to characterize longitudinal differences in trace element concentrations because streambed sediment in Lake Pepin are known to have elevated trace element concentrations (Bailey and Rada, 1984; Wiener and others, 1984). Fish livers, however, were obtained from only one site in Lake Pepin (site 26, fig. 3, table 1). Sites on the Sauk, Crow, Rum, Minnesota, Namekagon, St. Croix, Vermillion, and Cannon Rivers (fig. 3, table 1) were chosen to integrate potential upstream sources of constituents within each individual basin and to integrate the effect each stream may have had on the trace element concentrations in the Mississippi or St. Croix Rivers.

Six sites were selected as indicator sites to assess the natural and anthropogenic factors that affect the occurrence of trace elements within the study unit. These sites were selected through a stratification process. This process included dividing the study unit into subareas with homogeneous characteristics (Stark and others, 1996), and superimposing the drainage-basin boundaries on the resulting strata. Three levels of stratification were used, (1) glacial-deposit composition, (2) texture of surficial glacial deposits, and (3) general land use and land cover. It was assumed that these factors have a major influence on the hydrology, water quality, and aquatic biology of streams.

The first level of stratification primarily was based on whether the composition of surficial glacial deposits was calcareous or siliceous. Areas contained within the Wisconsin Driftless or Dissected Till Plains Sections of the Central Lowland Province were considered as a third separate stratum in this level of stratification because these sections generally were unglaciated during the last episode of Pleistocene glaciation.

The second level of stratification was based on texture of surficial glacial deposits. Areas of calcareous and siliceous surficial glacial deposits defined by the first level of stratification were further subdivided, based on whether the deposits generally were sorted (outwash and alluvium), or unsorted (till plains, and moraines). This level of stratification was not done for the Wisconsin Driftless and Dissected Till Plains Sections because of the different glacial history of these areas.

In the third level of stratification, each of the areas defined as a result of the first and second levels of stratification were further subdivided based on general land use and land cover. For this level of stratification, five types of land use and land cover were considered: (1) forest, (2) mixed agriculture and forest, (3) agriculture, (4) urban, and (5) wetlands and lakes. Urban land use was restricted to residential and commercial areas.

As a result of this stratification, there were 22 potential stratification combinations within the study unit (Stark and others, 1996). The six most dominant types of stratification combinations were selected for sampling based on areal extent within the study unit. These six stratification combinations represent: (1) agricultural land use/land cover on sorted surficial glacial deposits, (2) agricultural land use/land cover on unsorted surficial glacial deposits, (3) urban land use/land cover on sorted surficial glacial deposits, (4) urban land use/land cover on unsorted surficial glacial deposits, (5) forested land use/land cover on sorted surficial glacial deposits, and (6) forested land use/land cover on unsorted surficial glacial deposits.

Sites were selected to represent each of the six main stratification combinations (sites 4, 10, 13, 15, 17, and 20; fig. 3; table 1). Sites 4 and 13, located on the North Fork Crow and Little Cobb Rivers, represent stratification combinations (1) and (2), respectively. Sites 10 and 15, located on Shingle and Nine Mile Creeks, represent stratification combinations (3) and (4), respectively. And lastly, sites 17 and 20, located on the Namekagon and Kettle Rivers, respectively represent stratification combinations (5) and (6).

Two additional sites on Shingle Creek (sites 9 and 11) (fig. 3, table 1) also were sampled to characterize the longitudinal distribution of trace elements in a stream within the TCMA. Cedar Creek (site 6) (fig. 3, table 1) was sampled as a reference site in the Northern Central Hardwood Forests ecoregion to meet NAWQA Program objectives on the National level. Ecoregions are areas with relative homogeneity in ecological systems (Omernick and Gallant, 1988).

Sample Collection and Analytical Methods

Streambed-sediment sampling procedures for the NAWQA Program are described in detail by Shelton and Capel (1994) and are described here briefly. To minimize seasonal variability, each site was sampled in the summer or fall when streamflows typically are low compared to other times of the year. Streambed sediment were sampled along an approximately 300-ft reach at each site. Samples generally were not collected near obvious point sources of contaminants, such as wastewater treatment plant outfalls, storm sewer outfalls, or bridges. At each site, approximately 5 to 10 depositional zones that contained fine-grained sediment were targeted for sampling. Samples were collected from approximately the top 1 in. of wetted streambed sediment to obtain the most recently deposited material. At wadeable sites, streambed sediment were collected using either an acid-rinsed Teflon tube or Pyrex watch glass. At nonwadeable sites, streambed sediment cores were obtained using an Ekman dredge. Subsamples from approximately the top 1 in. of the dredged material were taken using either an acid-rinsed Pyrex watch glass or Teflon scoop. Care was taken to extract subsamples only from the undisturbed sample in the center of the dredge, avoiding the metal edges. Subsamples were composited in an acid-rinsed Pyrex container. To minimize biases among sites due to grain-size effects, sediments were wet sieved with native stream water through a 62-micron-mesh nylon-sieve cloth. After sieving, samples were transported on ice to a controlled setting, and

allowed to settle for approximately 2–3 days while refrigerated. After the sediments had settled, the liquid was decanted to within about 0.5 in. of the sediment/water interface and shipped to the USGS National Water-Quality Laboratory in Arvada, Colorado, for analysis.

Analytical techniques used to determine total trace element concentrations in streambed sediment are described in detail by Arbogast (1990). A total of 47 trace elements and other constituents were analyzed (table 2). All samples were air dried in the lab prior to analysis. Most trace element concentrations were determined using inductively-coupled plasma spectroscopy. Cadmium and silver concentrations were measured using graphite furnace atomic-absorption spectrophotometry. Antimony, arsenic, and selenium concentrations were measured using continuous-flow hydride generation atomic-absorption spectrophotometry. Mercury concentrations were analyzed using cold-vapor atomic-absorption spectrophotometry. Uranium and thorium were determined by delayed neutron activation. Total carbon and sulfur concentrations were determined using an automated carbon and sulfur analyzer. Inorganic carbon concentrations were analyzed by coulometric titration. Organic carbon concentrations subsequently were determined by difference.

Fish liver collection procedures are described in detail by Crawford and Luoma (1993). Based on expected occurrence throughout the study unit, common carp (*Cyprinus carpio*) and white sucker (*Catostomus commersoni*) were the taxa selected for analysis from a National Target Taxa list developed by Crawford and Luoma (1993). Shorthead redhorse (*Moxostoma macrolepidotum*) or golden redhorse (*Moxostoma erythrurum*) were the alternative taxa collected at sites where carp or white sucker were not present. Livers were targeted for analysis to maximize detection of trace elements. Fish were obtained by electroshocking. Approximately five to eight fish were collected at each site and an effort was made to collect specimens of approximately the same size. All fish specimens were measured, weighed, and sex determined before they were dissected. Scale samples also were collected at most sites for age determination. To avoid contamination, a separate scalpel was used to open the body cavity of each fish, and another scalpel was used to extract the liver. All fish livers for each individual species at a site, were composited into one sample of 5 to 10 grams and shipped on dry ice to the USGS National Water-Quality Laboratory for analysis.

The analytical methods used to determine trace element concentrations in fish liver samples are described in detail by Hoffman (1996). A total of 22 trace elements were analyzed (table 2). Prior to analysis, fish liver samples were decomposed using a low-temperature (85ºF) nitric acid and hydrogen peroxide digestion. After digestion, the samples were evaporated to incipient dryness, reconstituted with 5 percent nitric acid, and filtered to remove insoluble particles. The resulting solution was diluted to a known volume for analysis. Most trace element concentrations, except mercury, were determined by either inductively coupled plasma-mass spectrometry or inductively coupled plasma-atomic emission spectroscopy. Mercury concentrations were determined by cold vapor-atomic absorption spectrophotometry.

Quality Assurance

Quality assurance samples were collected to assess variability in the streambed sediment and fish liver processing or analysis procedures, and intra-site variability among streambed sediment from different depositional zones in the same stream reach. To assess the variability in streambed sediment processing or analysis procedures, three split-replicate streambed sediment samples were collected from Shingle Creek (site 10, fig. 3, table 1) because trace element concentrations were expected to be relatively large at this site relative to other locations sampled in the study unit. Replicate fish liver samples were collected from the Mississippi River at Lake Pepin (site 26, fig. 3, table 1) to assess the variability in the fish liver processing and analysis procedures. To assess intra-site variability among sediments from different depositional zones in the same stream reach, streambed sediment was collected, individually processed, and analyzed separately from near the right and left sides of the Crow River (site 5, fig. 3, table 1).

TRACE ELEMENTS IN STREAMBED SEDIMENT

All trace elements analyzed in streambed sediment were detected except bismuth, europium, gold, holmium, molybdenum, tantalum, and tin (table 3). The trace elements with the greatest variability among the sites, as indicated by the coefficient of variation (Devore and Peck, 1986) in table 3, were antimony, arsenic, cadmium, copper, lead, manganese, mercury, niobium, silver, sulfur, and zinc. Censored values were handled in the computation of the coefficient of variation by substituting one-half the reporting limit for each censored value. Concentrations of trace elements in streambed sediment collected near the right and left sides of the Crow River (site 5, fig. 3, table 1) and from the North Fork Crow and Little Cobb Rivers in 1995 and 1996 (sites 4 and 13, fig. 3, table 1) were averaged for all analyses in this report to eliminate weighting the results to more frequently sampled sites. Averaging the trace element concentrations determined at these sites is unlikely to substantially affect the results presented in this report. Quality assurance sampling indicated little variation in trace element concentrations, and concentrations in these primarily agricultural areas were not expected to have any substantial change during the time period of this study.

Streambed sediment sampling sites were grouped using principal components analysis (Flury and Riedwyl, 1988) because trace element concentrations among the sites were expected to have similar patterns related to the composition of the surficial glacial deposit or land use and land cover of the study unit. Principal components analysis (PCA) is a multivariate statistical technique that is used to decompose a data set containing many variables for each observation or site into a few principal components (Daultrey, 1976; Flury and Riedwyl, 1988). Each principal component is a weighted linear combination of all the variables in a data set. The first principal component accounts for the largest percentage of the variance in a data set. The second princi-

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Table 2. Trace elements and other selected constituents analyzed in streambed sediment and fish livers, 1995–96

[NA, not analyzed;%, percent by weight]

Constituent	Method reporting limit (units are micrograms per grams unless otherwise noted)	
	Streambed sediment	Fish livers
Trace elements		
Aluminum	0.005%	1
Antimony	0.1	[1]0.1–0.66
Arsenic	0.1	[1]0.1–0.66
Barium	1	0.1
Beryllium	1	[1]0.1–0.66
Bismuth	10	NA
Boron	NA	0.2
Cadmium	0.1	[1]0.1–0.66
Cerium	4	NA
Chromium	1	[1]0.33–0.5
Cobalt	1	[1]0.1–0.66
Copper	1	0.5
Europium	2	NA
Gallium	4	NA
Gold	8	NA
Holmium	4	NA
Iron	1	0.005%
Lanthanum	2	NA
Lead	4	[1]0.1–0.66
Lithium	2	NA
Manganese	4	0.1
Mercury	0.02	[1]0.01–0.1
Molybdenum	2	0.1
Neodymium	4	NA
Nickel	2	[1]0.1–0.66
Niobium	4	NA
Scandium	2	NA
Selenium	0.1	0.1
Silver	0.1	[1]0.1–0.66
Sodium	0.005%	NA
Strontium	2	0.1
Tantalum	40	NA
Thorium	1	NA
Titanium	0.005%	NA
Tin	5	NA

Table 2. Trace elements and other selected constituents analyzed in streambed sediment and fish livers, 1995–96(Continued)

[NA, not analyzed;%, percent by weight]

Constituent	Method reporting limit (units are micrograms per grams unless otherwise noted)	
	Streambed sediment	Fish livers
Uranium	0.05	[1]0.1–0.66
Vanadium	2	[1]0.1–0.66
Ytterbium	1	NA
Yttrium	2	NA
Zinc	4	0.5
Other constituents		
Calcium	0.005%	NA
Carbon, inorganic	0.01%	NA
Carbon, organic[2]	0.01%	NA
Carbon, total	0.01%	NA
Magnesium	0.005%	NA
Phosphorus	0.005%	NA
Potassium	0.05%	NA
Sulfur	0.05%	NA

[1.] The method reporting limit for this constituent varied among sites and species.
[2.] The concentration of this constituent was determined by subtracting the inorganic carbon concentration from the total carbon concentration.

pal component is not correlated to the first principal component and accounts for the largest percentage of the remaining variance in a data set. This pattern of determining principal components is repeated until all of the variance in a data set is accounted for by principal components. Typically, the first two or three principal components explain most of the variance in a data set.

Principal component loadings and principal component scores also are calculated as part of a PCA. Principal component loadings (hereinafter referred to as loadings) are the covariances of the original variables with the principal components. Loadings are calculated for each variable/principal component combination in a data set. The loadings are used to interpret each of the principal components in terms of the original variables in a data set. For each principal component, the variables with the largest loadings are examined to give the principal component a descriptive name. Principal component scores (hereinafter referred to as scores) are the values of the principal components. Scores are calculated for each site/principal component combination in a data set. The scores can be used to classify sites and are often used in cluster analysis (Gauch, 1982) for this purpose.

The initial principal components obtained from a PCA are often difficult to interpret (Wilkinson and Stenson, 1997). To facilitate interpretation of PCA results, the principal components can be rotated so each variable in a data set is associated with fewer principal components. Common rotations used include varimax, equamax, quartimax, and oblique (Wilkinson and Stenson, 1997).

In this study, PCA was done using a varimax rotation with most constituents analyzed, except inorganic carbon, organic carbon, total carbon, thorium, and uranium. These constituents were not included because they were not analyzed at every site (table 3). Censored values were handled by substituting one-half the reporting limit for each censored value. Constituent concentrations were negative-reciprocal-square root transformed to make them more normally distributed because distributions of some of the constituent concentrations, such as lead and zinc, were heavily skewed to the greater concentrations. Application of the Kolmogorov-Smirnov test (Wilkinson, 1997) showed all of the transformed concentration values, with the exception of barium, potassium, lithium, neodymium, and ytterbium, were normally distributed at the five percent confidence level.

The first three principal components (table 4) explained the majority (60 percent) of the variability in the concentration of trace elements in streambed sediment across the study unit. The first and third principal components were interpreted as describing the natural variability in elemental composition of streambed sediment as a result of the surficial geology of the study unit

The first principal component explained 25 percent of the total variance in the data set. The constituents with large, positive loadings for principal component 1 were aluminum, barium, beryllium, calcium, cerium, gallium, lanthanum, lithium, magnesium, neodymium, potassium, and strontium (table 4). These results were interpreted as describ-

Table 3. Summary statistics for trace elements and other selected constituents in streambed sediment at all sites sampled in the Upper Mississippi River Basin study unit, 1995–96

[Units are micrograms per gram unless otherwise noted;%, percent by weight; nd, not detected]

Constituent	Number of samples	Median	Coefficient of variation	Minimum	Maximum
Aluminum	27	5.0%	0.223	2.2%	6.4%
Antimony	27	1.00	0.616	0.30	3.00
Arsenic	27	7.7	0.596	5.3	25
Barium	27	520	0.162	310	740
Beryllium	27	1	0.493	<1	2
Bismuth	27	All values less than 10 µg/g	nd	nd	nd
Cadmium	27	0.7	0.590	0.3	2.2
Calcium	27	3.4%	0.615	1.2%	11%
Carbon, inorganic	24	0.81%	0.817	0.01%	3.21%
Carbon, organic	24	4.66%	0.577	1.43%	16.0%
Carbon, total	25	5.62%	0.483	2.98%	16.1%
Cerium	27	61	0.198	27	74
Chromium	27	71	0.214	31	89
Cobalt	27	13	0.265	9.5	23
Copper	27	28	0.634	8	87
Europium	27	All values less than 2 µg/g	nd	nd	nd
Gallium	27	11	0.321	4	19
Gold	27	All values less than 8 µg/g	nd	nd	nd
Holmium	27	All values less than 4 µg/g	nd	nd	nd
Iron	27	4.1%	0.320	2.4%	8.7%
Lanthanum	27	32	0.217	15	40
Lead	27	23	1.311	12	300
Lithium	27	20	0.340	9	40
Magnesium	27	1.2 %	0.396	1.2%	2.3%
Manganese	27	2000	0.625	560	6600
Mercury	27	0.09	0.620	0.03	0.32
Molybdenum	27	All values less than 2 µg/g	nd	nd	nd
Neodymium	27	24	0.240	10	32
Nickel	27	29	0.260	11	47
Niobium	27	6	1.161	< 4	55
Phosphorus	27	0.15%	0.498	0.08%	0.48%
Potassium	27	1.30%	0.232	0.5%	1.5%
Scandium	27	8	0.202	4	12
Selenium	27	1.3	0.415	0.6	2.8
Silver	27	0.30	0.570	0.15	0.80
Sodium	27	0.76%	0.322	0.36%	1.30%
Strontium	27	140	0.244	64	220
Sulfur	27	0.16 %	0.787	< 0.05%	0.78%
Tantalum	27	All values less than 40 µg/g	nd	nd	nd
Thorium	24	9.0	0.287	< 5	12
Tin	27	All values less than 5 µg/g	nd	nd	nd
Titanium	27	0.27%	0.305	0.13%	0.60%

Table 3. Summary statistics for trace elements and other selected constituents in streambed sediment at all sites sampled in the Upper Mississippi River Basin study unit, 1995–96

[Units are micrograms per gram unless otherwise noted;%, percent by weight; nd, not detected]

Constituent	Number of samples	Median	Coefficient of variation	Minimum	Maximum
Uranium	24	2.65	0.180	1.30	3.40
Vanadium	27	90	0.267	34	150
Ytterbium	27	2	0.257	< 1	3
Yttrium	27	18	0.167	8	24
Zinc	27	104	0.697	65	490

ing streambed sediment which was strongly influenced by surficial glacial deposits from by the Des Moines or Wadena Lobes. These two glacial lobes advanced from the west and northwest, and their deposits cover much of the study unit. Theses deposits are generally calcareous in composition with parent materials of limestone, shale, and granite (Ojakangas and Matsch, 1982). Major constituents of limestone and dolomite are calcium, magnesium, and carbonate, and commonly include barium and strontium. Contributions from granite would contain substantial amounts of quartz and feldspar minerals, which would contribute aluminum, calcium, potassium, and silicon. Feldspar minerals also may contain small quantities of barium, cerium, europium, gallium, lanthanum, lead, lithium, strontium, and zinc (Henderson, 1982). Shale commonly consists of aluminum, iron, magnesium, potassium, and silicon, with minor amounts of titanium and sodium. Therefore, many of those constituents with the greatest loading for principal component 1 would be associated with surficial material from the calcareous glacial deposits.

The third principal component explained 21 percent of the total variance in the streambed sediment data set. The elements with the large, positive loadings for principal component 3 were chromium, copper, nickel, scandium, titanium, vanadium, ytterbium, and yttrium (table 4). These results were interpreted as describing those streambed sediment which were strongly influenced by the Superior or Rainy Lobes. These two glacial lobes, which traversed the northeastern part of the study unit, deposited glacial material characterized as siliceous with primarily a basaltic source (Ojakangas and Matsch, 1982). The major minerals in basalt are olivine, pyroxene, plagioclase, and iron-titanium oxides. Major constituents of olivine and pyroxene include iron, calcium, magnesium, and silicon. Iron-titanium oxides are very resistant to weathering and often are concentrated in fluvial sediments. Pyroxene, olivine, and iron-titanium oxides also may have trace amounts of cobalt, chromium, manganese, nickel, scandium, vanadium, and ytterbium (Henderson, 1982). Plagioclase is primarily calcium, sodium, aluminum, and silicon. Most of the elements identified by principal component 3 are associated with basalts. The high loading of copper may reflect the widespread copper enrichment found in basalts in the northeastern part of the study unit (Nicholson and others, 1992).

Scores (table 5) were consistent with these interpretations of principal components 1 and 3. Sites with the greatest scores for principal component 1 (sites 14, 16, 25–27; fig. 2; tables 1 and 5) were located in parts of the study unit where surficial glacial deposits are calcareous in composition (fig. 3 and table 1). In contrast, most sites with the lowest scores for principal component 1 (sites 6, and 17–19) were located in the St. Croix River Basin (fig. 2, tables 1 and 5) where surficial glacial deposits are siliceous and contain few carbonate minerals. Sites with the greatest scores for principal component 3 (sites 17–22, fig. 2, tables 1 and 5) were located where surficial glacial deposits are calcareous. The sampling site on Cedar Creek (site 6, fig. 2, tables 1 and 3) had low scores for both principal components 1 and 3. This was interpreted as describing sediment that was enriched in organic matter with respect to the other sites sampled as part of this study. Unfortunately, this hypothesis could not be confirmed or denied because there was not enough sediment collected at this site for an organic carbon analysis to be performed. However, conditions at this site (slow-moving water with numerous macrophytes growing in the streambed) indicated the site may be enriched in organic matter.

The second principal component explained 14 percent of the total variance in the data set and had large, positive loadings from antimony, arsenic, cadmium, copper, lead, mercury, nickel, and zinc (table 4). Large, positive loadings from these constituents indicated this component described streambed sediment with anthropogenic contamination because sites with the greatest scores were located within or near urban areas in the study unit—the TCMA; Hudson, Wisconsin; and Grand Rapids, Minnesota (sites 1, 9–11, 15, and 22; fig. 2; tables 1 and 5). At these sites, median concentrations of these constituents in the streambed sediment were about 1.5 to 5 times greater than the median concentration for all sites combined (table 6). There were also large, negative scores for principal component 2 for sites on the North Fork Crow, Crow, Little Cobb, and Kettle Rivers (sites 4, 5, 13, and 20; fig. 2; tables 1 and 5), which indicates some of the smallest concentrations of antimony, arsenic, cadmium, copper, lead, mercury, nickel, and zinc were measured at these locations. Median concentrations at these locations were smaller than those determined at all sites sampled and those

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Table 4. Principal component loadings for the first three principal components, from principal component analysis of trace element and other selected constituent concentrations in streambed sediment in part of the Upper Mississippi River Basin study unit, 1995–96.

Constituent	Principal component 1	Principal component 2	Principal component 3
Aluminum	0.877	-0.015	0.408
Antimony	0.159	0.850	0.080
Arsenic	-0.079	0.569	-0.432
Barium	0.836	-0.053	-0.347
Beryllium	0.624	-0.004	0.036
Cadmium	0.044	0.494	-0.249
Calcium	0.528	0.176	-0.308
Cerium	0.840	0.098	0.419
Chromium	0.099	0.435	0.839
Cobalt	-0.017	0.421	0.389
Copper	-0.103	0.670	0.585
Gallium	0.604	-0.066	0.470
Iron	-0.280	0.100	-0.158
Lanthanum	0.897	0.035	0.310
Lead	0.014	0.872	0.042
Lithium	0.872	-0.079	0.279
Magnesium	0.766	0.224	0.247
Manganese	-0.026	0.162	-0.035
Mercury	-0.183	0.635	0.134
Neodymium	0.590	0.031	0.517
Nickel	0.462	0.486	0.612
Niobium	0.133	0.038	0.189
Phosphorus	0.396	0.320	-0.324
Potassium	0.826	0.118	0.393
Scandium	0.402	0.014	0.895
Selenium	-0.439	0.329	0.013
Silver	0.091	0.369	0.062
Sodium	0.322	0.135	0.088
Strontium	0.839	0.013	-0.195
Sulfur	-0.414	0.448	-0.322
Titanium	0.174	0.001	0.822
Vanadium	0.096	0.027	0.910
Ytterbium	0.555	0.008	0.644
Yttrium	0.244	0.020	0.939
Zinc	0.158	0.814	0.195

determined from sites located near the urban areas of the study unit (table 6).

The distributions of the concentrations of antimony, arsenic, cadmium, copper, lead, mercury, nickel, niobium, and zinc in the streambed sediment are discussed in detail in this section of the report. All of these constituents, with the exception of niobium, were identified by the PCA as having probable anthropogenic origins. Antimony is used in lead storage batteries, mixed with other metals into alloys, added to textiles and plastics as a fire retardant, and also is a component of paints, ceramics, and fireworks (Agency for Toxic Substances and Disease Registry, 1992). Arsenic is used as a wood preservative (chromated copper arsenate) and in the past has been used as a pesticide. Cadmium is used in batteries,

Table 5. Site scores for principal components 1, 2, and 3; from principal component analysis of element concentrations in streambed sediment in part of the Upper Mississippi River Basin study unit, 1995–96.

Map identifier (figures 2 and 3)	USGS site identifier	Principal component 1	Principal component 2	Principal component 3
1	05211000	0.380	1.686	-0.601
2	05263500	0.501	-0.553	0.301
3	05270380	0.381	-0.369	-0.179
4	05276005	-0.395	-2.048	-0.578
5	05280400	0.606	-1.032	-0.674
6	05286290	-1.907	-0.786	-3.648
7	05287000	0.308	-0.294	-0.065
8	05288500	0.531	-0.559	0.478
9	05288695	0.064	1.787	-0.219
10	05288705	-0.469	1.669	-0.734
11	05288710	0.250	1.971	-0.283
12	05288730	0.490	0.028	0.502
13	05320270	0.395	-1.238	0.481
14	05330000	0.800	-0.569	-0.725
15	05330902	0.457	1.236	-0.168
16	05331570	0.786	-0.358	-0.503
17	05331833	-2.429	0.321	0.846
18	05331873	-2.849	-0.089	1.288
19	05333500	-1.206	-0.021	0.924
20	05336180	0.210	-1.028	1.428
21	05339770	-0.462	-0.704	0.812
22	05341552	-0.249	1.031	0.944
23	05345000	0.637	0.223	-1.140
24	05355090	0.586	-0.422	-0.213
25	443334092205201	0.886	0.272	0.691
26	442912092174201	0.950	-0.168	0.683
27	442633092130801	0.713	0.017	0.351

Table 6. Median antimony, arsenic, cadmium, copper, lead, mercury, nickel, and zinc concentrations in streambed sediment from the Upper Mississippi River Basin study unit, 1995–96

[Units are micrograms per gram]

Trace element	All sites combined	North Fork Crow, Crow, Little Cobb, and Kettle River sites[1]	Sites located near urban areas in the study unit[2]
Antimony	1	0.58	2
Arsenic	7.7	5.6	11.5
Cadmium	0.7	0.5	1.75
Copper	28	19	60
Lead	23	16	170
Mercury	0.09	0.05	0.13
Nickel	29	25	38
Zinc	104	93	360

[1.] Sites 4, 5, 13, and 20 (figure 2 and table 1)
[2.] Sites 1, 9–11, 15, and 22 (figure 2 and table 1)

pigments, metal coatings, and plastics. Copper is used in wire, pipe, mixed with other metals to form alloys, and is used in chemicals such as copper sulfate. Lead has been used in the past in gasoline, paint, and pipe solder (Agency for Toxic Substances and Disease Registry, 1993), but these uses have decreased substantially. Lead also is used in batteries and ammunition. Nickel is used in the manufacturing of stainless steel, combined with other metals to form alloys (Agency for Toxic Substances and Disease Registry, 1996). Mercury is used in batteries, fluorescent lights, thermometers, thermostats, barometers, and dental amalgam. In the past, mercury also has been used in pigments and as a fungicide for seeds, and has been added to latex paint to prevent mildew and used as a biocide in paper making. Nickel compounds also are used in nickel plating, to color ceramics, and in batteries. Zinc is used in coatings to prevent corrosion, batteries, mixed with other metals to make alloys such as bronze and brass, and also is used in the production of rubber, paints, wood preservatives, and ointments. Most of these metals also may be emitted to the atmosphere as a result of the combustion of fossil fuels or refuse incineration, and may eventually reach streams by atmospheric deposition.

Exposure to most of these metals can cause health problems in humans and aquatic biota. The bioavailability of metals associated with the streambed sediment is not completely known. However, under the appropriate physical conditions, such as low dissolved oxygen concentrations, metals can be released from the sediment to the water. Arsenic is extremely toxic to humans and aquatic biota. Ingestion of this element may damage the reproductive and cardiovascular systems (Morton and Dunnette, 1994). Dissolved cadmium concentrations as low as 1 microgram per liter (µg/L) may be acutely toxic to some species of fish (U.S. Environmental Protection Agency, 1986). Dissolved copper concentrations as low as about 6 µg/L may be acutely toxic to some types of aquatic biota (U.S. Environmental Protection Agency, 1986). Exposure to lead may affect almost every organ and system in humans, with the central nervous system being the most sensitive (Agency for Toxic Substances and Disease Registry, 1993). However, exposure to lead is most dangerous to young children. Harmful effects of lead in young children include decreased mental ability, learning disabilities, and reduced growth. Exposure to increased concentrations of mercury may permanently damage the brain and kidneys (Agency for Toxic Substances and Disease Registry, 1994), and concentrations as low as about 2 µg/L in the water may be acutely toxic to some forms of aquatic life (U.S. Environmental Protection Agency, 1986).

The baseline concentration is the constituent concentration found at relatively unaffected locations at a particular time, such as the beginning of a study. Baseline antimony, arsenic, cadmium, copper, lead, nickel, and zinc concentrations were estimated using probability plots of the distribution (Velz, 1984). This method assumes baseline and contaminated samples have different underlying distributions, such that reasonable baseline concentrations may be represented by the concentration at the first break in the slope of the probability plot. Baseline mercury concentrations were not estimated because no break in slope could be readily discerned from a probability plot of the concentration data.

Antimony concentrations were greatest in streambed sediment from the Mississippi River at Grand Rapids, Minnesota (site 1); the Sauk River at Richmond, Minnesota (site 3); Shingle Creek (sites 9–11); Nine Mile Creek near James Circle at Bloomington, Minnesota (site 15); the St. Croix River at Hudson, Wisconsin (site 22); and in Lake Pepin near Frontenac, Minnesota (site 25) (fig. 4). Concentrations at these sites ranged from about 2 to 3 micrograms per gram (µg/g) and were about two to three times the baseline concentration. The greatest concentrations of antimony, 3 µg/g, were measured in streambed sediment from Shingle Creek at Zane Avenue at Brooklyn Park, Minnesota (site 9) and at 46th Street in Minneapolis, Minnesota (site 11), and in Lake Pepin near Frontenac, Minnesota (site 25).

Concentrations of arsenic were greatest in Cedar Creek near Coopers Corner, Minnesota (site 6), Shingle Creek (sites 9–11), and the Vermillion River near Empire, Minnesota (site 23). At these sites, concentrations ranged from 14 to 25 µg/g and generally were about two times the baseline concentration. In Shingle Creek, arsenic concentrations in the streambed sediment were greater at sites located at Zane Avenue at Brooklyn Park, Minnesota (site 9) and at 46th Street in Minneapolis, Minnesota (site 11) compared to those measured at Queen Avenue in Minneapolis, Minnesota (site 10).

Cadmium concentrations were greatest in streambed sediment from Shingle Creek (sites 9–11); the Minnesota River near Jordan, Minnesota (site 14); Nine Mile Creek near James Circle at Bloomington, Minnesota (site 15); the Mississippi River at Nininger, Minnesota (site 16); and in Lake Pepin (sites 25–27) (fig. 4). Concentrations at these sites were about two to four times the baseline concentration. Of these sites, the greatest concentrations of cadmium, 1.7 to 2.2 µg/g, were measured in streambed sediment from Shingle Creek.

Copper concentrations were greatest in streambed sediment from Shingle Creek (sites 9–11); Nine Mile Creek near James Circle at Bloomington, Minnesota (site 15); the Namekagon River at Leonards, Wisconsin (site 17) and the Namekagon River above Spring Lake Creek near Hayward, Wisconsin (site 18); and the St. Croix River at Hudson, Wisconsin (site 22). At these sites, copper concentrations in the streambed sediment ranged from 37 to 87 µg/g. Concentrations in Shingle Creek and the St. Croix River at Hudson, Wisconsin were about two times the baseline concentration. In Shingle Creek, concentrations in the streambed sediment were greater at the sites located at Zane Avenue at Brooklyn Park, Minnesota (site 9) and at 46th Street in Minneapolis, Minnesota (site 11) compared to those measured at Queen Avenue in Minneapolis, Minnesota (site 10).

Lead concentrations were greatest in streambed sediment from the Mississippi River at Grand Rapids, Minnesota (site 1); Shingle Creek (sites 9–11); Nine Mile Creek near James Circle at Bloomington, Minnesota (site 15); and the St. Croix River at Hudson, Wisconsin (site 22). At these sites, lead concentrations ranged

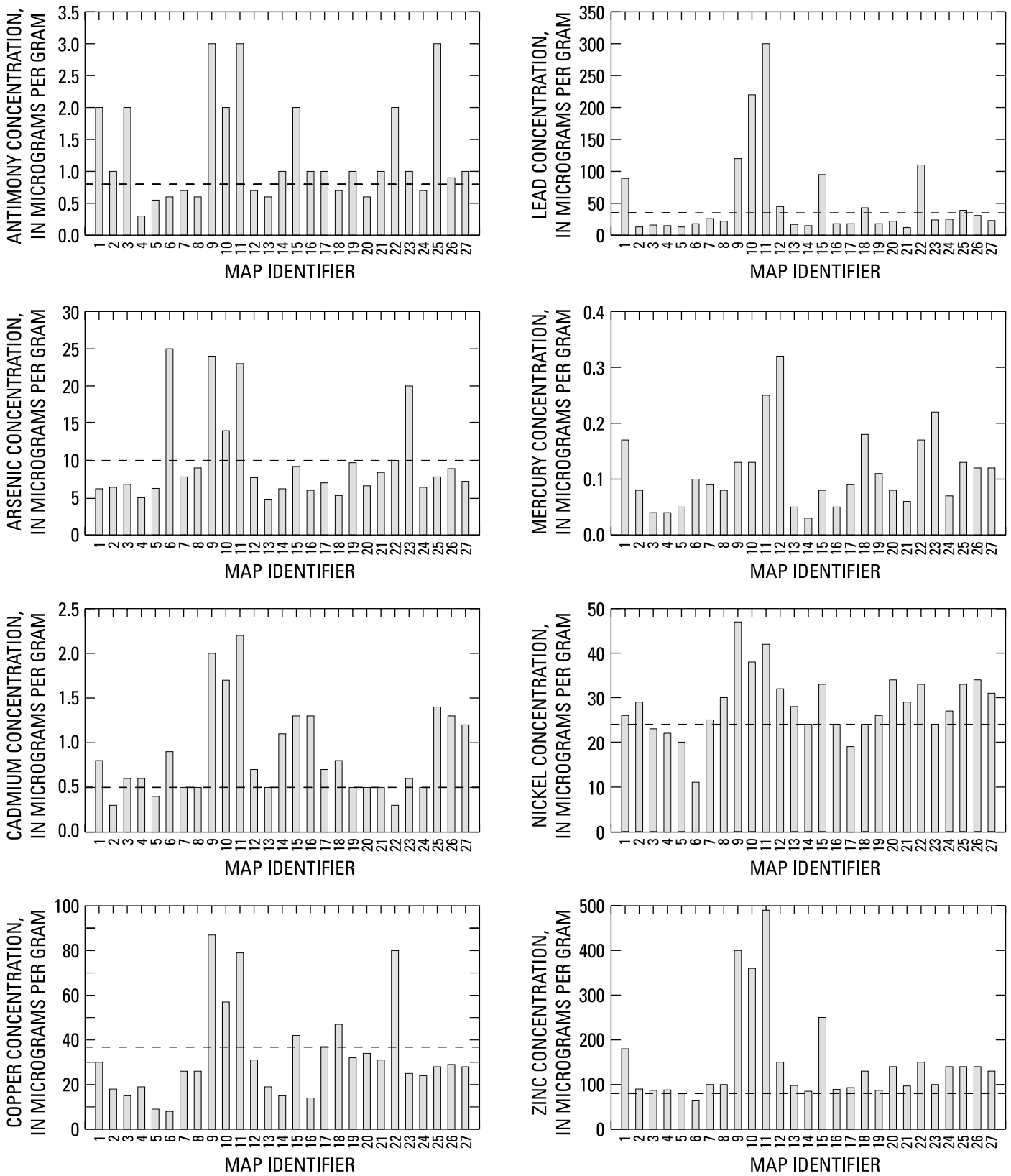

Figure 4.--Antimony, arsenic, cadium, copper, lead, mercury, nickel, and zinc concentrations in streambed sediment samples obtained from the Upper Mississippi River Basin study unit, 1995-96 [Dashed lines show baseline concentrations. [Map identifier corresponds to site in figures 2 and 3 and table 1].

from 89 to 300 µg/g and were about 2 to 10 times the baseline concentration. Lead concentrations measured along Shingle Creek increased in the downstream direction from 120 µg/g at Zane Avenue at Brooklyn Park, Minnesota (site 9) to 300 µg/g at 46th Street in Minneapolis, Minnesota (site 11). Concentrations in the sediment from Lake Pepin decrease in the downstream direction from 39 µg/g near Frontenac, Minnesota to 23 µg/g near Lake City, Minnesota (sites 25–27, fig. 4).

Concentrations of mercury were greatest in streambed sediment from the Mississippi River at Grand Rapids and Minneapolis, Minnesota (sites 1 and 12); Shingle Creek at 46th Street in Minneapolis, Minnesota (site 11); the Namekagon River above Spring Lake Creek near Hayward, Wisconsin (site 18); the St. Croix River at Hudson, Wisconsin (site 22); and the Vermillion River near Empire, Minnesota (site 23)(fig. 4). Mercury concentrations in streambed sediment from these sites ranged from 0.17 to 0.32 µg/g.

Nickel concentrations were greatest in streambed sediment from Shingle Creek (sites 9–11)(fig. 4). Concentrations measured in sediment from these sites ranged from 38 to 47 µg/g and generally were about two times the baseline concentration. Of these three sites, the greatest concentration was measured in sediment at Zane Avenue at Brooklyn Park, Minnesota (site 9) and the lowest concentration was measured at Queen Avenue in Minneapolis, Minnesota (site 10).

The niobium concentration in streambed sediment generally did not vary appreciably. However, a substantially elevated concentration, 55 µg/g, was measured in sediment from Shingle Creek at 46th Street in Minneapolis, Minnesota (site 11). This is more than five times greater than the baseline concentration of 10 µg/g.

Zinc concentrations were greatest in streambed sediment from the Mississippi River at Grand Rapids, Minnesota (site 1); Shingle Creek (sites 9–11); and Nine Mile Creek near James Circle at Bloomington, Minnesota (site 15)(fig. 4). At these sites, concentrations ranged from 180 to 490 µg/g and were about two to five times the baseline concentration. In Shingle Creek, zinc concentrations were greater in streambed sediment obtained from Zane Avenue at Brooklyn Park, Minnesota (site 9) and at 46th Street in Minneapolis, Minnesota (site 11) compared to those measured at Queen Avenue in Minneapolis, Minnesota (site 10).

Concentrations in streambed sediment combined with results of the PCA further indicated that concentrations of antimony, cadmium, copper, lead, nickel, and zinc were strongly influenced by anthropogenic factors. Elevated concentrations of these trace elements generally occurred at sites located within or near urban areas in the study unit. A recent coring study also showed an increase in concentrations of these trace elements, with the exception of antimony, which was not measured, in the sediment from two TCMA lakes, representing the period when the basins surrounding the lakes were urbanized (P.C. Van Metre, U.S. Geological Survey, written commun., 1998). The distribution of cadmium in the streambed sediment throughout the study unit also was consistent with studies of cadmium in soils from urban areas in Minnesota (Mielke and others, 1991), which determined that the soil cadmium content varied directly with city size and the greatest concentrations of cadmium were measured in Minneapolis soils.

The greatest concentrations of most of these trace elements tended to occur at sites located on Shingle Creek (sites 9–11, fig. 4). The longitudinal pattern in lead concentrations in Shingle Creek probably reflects the past use of leaded gasoline, pesticides, or paints, especially considering that the two most downstream sites on Shingle Creek were located in areas with greater population densities and older residential development. Of the three sites located on Shingle Creek, concentrations of antimony, arsenic, cadmium, copper, and zinc were least in streambed sediment collected from the site located at Queen Avenue (site 10, fig. 4). Lower concentrations at this site may be the result of locally lower inputs of trace elements or dilution by relatively uncontaminated sediments. There also may be less sorption of trace elements to the sediment at this location because the iron content of the sediment was lower compared to the other two sites on Shingle Creek.

Increased arsenic concentrations in sediments from Cedar Creek near Coopers Corner, Minnesota (site 6); Shingle Creek at Zane Avenue in Brooklyn Park, Minnesota (site 9); and the Vermillion River near Empire, Minnesota (site 23)(fig. 4) may have been the result of weathering from a local source of sulfide minerals or the preferential sorption of arsenic onto iron hydroxide coatings on sediments. For these three sites, greater arsenic concentrations corresponded with greater iron content (5.7 to 8.7 percent). It is possible that the breakdown of pyrite, an iron sulfide mineral, may have contributed both arsenic and iron to these sites, or that the presence of abundant iron hydroxide in the sediment may have preferentially bound arsenic to the sediment.

The pattern of cadmium concentrations in streambed sediment from the Mississippi River and Lake Pepin indicated inputs of this element into the river from the TCMA. This pattern also was consistent with results published by Beauvais and others (1995) who determined cadmium concentrations in bulk sediments were greater in Navigation Pools 2, 3, and 4 compared to other downstream locations. Navigation pools are defined as the reach of the Mississippi River between two locks and dams with the number of the navigation pool corresponding to the lock and dam at the downstream end. For example, Navigation Pool 2 is located between Locks and Dams 1 and 2. The longitudinal pattern of lead concentrations in bottom sediment from Lake Pepin probably reflects the settling out of particulate matter in the upstream part of the lake.

In the St. Croix River, concentrations of antimony, copper, lead, mercury, nickel, and zinc were increased in the streambed sediment at Hudson, Wisconsin (site 22, fig. 4) relative to the other two sites sampled on this river (sites 19 and 21, fig. 4). These results were consistent with an analysis of historical data collected in the St. Croix River Basin (Troelstrup and others, 1993), which determined trace element concentrations in the water were greater in the most

downstream reaches of the St. Croix River, which are more urbanized.

It is unknown why the antimony concentration in streambed sediment obtained from the Sauk River at Richmond, Minnesota (site 3, fig. 4) was large relative to other nonurban areas. There may be either a natural or local anthropogenic source of antimony in this area.

TRACE ELEMENTS IN FISH LIVERS

Fish were collected at 25 of the 27 sites sampled for streambed sediment—only one site was sampled in Lake Pepin. An effort was made to collect fish of the same size. However, fish collected at the stream sites draining smaller areas tended to be smaller (table 7).

All of the trace elements analyzed (table 2) in fish livers in the study unit were detected except antimony, beryllium, cobalt, and uranium (table 8). Censored values for constituents with only one reporting limit were handled in the computation of the summary statistics in table 8 by setting each censored value to one-half the method reporting limit. Method reporting limits varied by site and species of fish analyzed for arsenic, cadmium, chromium, lead, mercury, nickel, silver, and vanadium. In many instances, the method reporting limit for a given site was two to three times greater than the noncensored values for other sites. Censored values for these constituents were handled in the computation of summary statistics in table 8 by arbitrarily setting each censored value to one-half the lowest method reporting limit.

Concentrations of copper, iron, manganese, and zinc, which are essential for metabolism, were greater than the other constituents analyzed in fish livers (table 8). Ranges for concentrations of arsenic, cadmium, chromium, copper, lead, mercury, selenium, and zinc in common carp and white sucker livers were similar to those measured in 20 other NAWQA studies across the United States from 1992 through 1995 (Rod Deweese, U.S. Geological Survey, oral commun., 1999). No data were available from these 20 other NAWQA studies on the concentrations of these constituents in redhorse livers to compare with data obtained in the UMIS study unit.

Arsenic was detected in fish livers from 14 of the 25 sites sampled in the study unit (fig. 5). The greatest concentrations were measured in carp livers obtained from the central point of Lake Pepin (site 26) and the St. Croix River at Hudson, Wisconsin (site 22); and in shorthead redhorse livers from the Crow River below State Highway 101 at Dayton, Minnesota (site 5). In the Mississippi River, arsenic was detected in fish livers from most of the sites sampled except the northernmost site located at Grand Rapids, Minnesota (site 1). Arsenic also was detected in carp, redhorse, or white sucker livers from many of the tributaries to the Mississippi River— including the Sauk River at Richmond, Minnesota (site 3); Crow River below State Highway 101 at Dayton, Minnesota (site 5); Rum River at Anoka, Minnesota (site 7); Little Cobb River near Beauford, Minnesota (site 13); Minnesota River near Jordan, Minnesota (site 14); St. Croix River near Danbury and at Hudson, Wisconsin (sites 19 and 22); Vermillion River near Empire, Minnesota (site 23); and the Cannon River at Lake Byllesby near Cannon Falls, Minnesota (site 24). Most of these streams drain agricultural areas, which indicates land use may affect arsenic concentrations in fish livers from the study unit. However, arsenic not being detected in fish livers from many sites in the study unit may have been an artifact of higher method reporting limits. The method reporting limit for arsenic varied among sites and samples (table 2). Method reporting limits may vary as a result of matrix effects, interferences with other elements, or sample size. At the sites where arsenic was not detected in the fish livers, the method reporting limits appeared to be relatively high. For example, arsenic was not detected in carp livers collected from Shingle Creek at Queen Avenue in Minneapolis, Minnesota (site 10, fig.6, table 1). However, the method reporting limit for this sample, (0.66 µg/g) was greater than most of the other detectable concentrations of arsenic in fish livers from the study unit. Arsenic concentrations in fish livers obtained from the study unit also appeared to be related to fish size. There were moderate correlations between arsenic concentrations and total fish length and weight (Kendall tau correlation coefficients were 0.538 and 0.528, respectively), which is consistent with other studies (Bohn and Fallis, 1978; and Bohn and McElroy, 1976), that reported arsenic concentrations in fish positively correlated with body size.

Cadmium was detected in fish livers from 17 of the 25 sites sampled (fig. 5). The greatest concentrations were measured in white sucker livers from the Minnesota River near Jordan, Minnesota (site 14); redhorse livers from the Crow River below State Highway 101 at Dayton, Minnesota (site 5); and carp livers obtained from the Little Cobb River near Beauford, Minnesota (site 13) and the St. Croix River at Hudson, Wisconsin (site 22). Similar to the results for arsenic, cadmium was detected in all of the Mississippi River sites sampled except the northernmost one located at Grand Rapids, Minnesota. Cadmium also was detected in fish livers obtained from most of the tributaries to the Mississippi River except in fish livers from Cedar Creek near Coopers Corner, Minnesota (site 6); the two upstream sites on Shingle Creek (sites 9 and 10), Nine Mile Creek near James Circle at Bloomington, Minnesota (site 15); both sites on the Namekagon River (sites 17 and 18), the St. Croix River near Danbury, Wisconsin (site 19); and the Kettle River near Kettle River, Minnesota (site 20). Cadmium concentrations in the fish livers were moderately correlated with total fish length and weight (Kendall tau correlation coefficients were 0.522 and 0.519, respectively), which is consistent with results from a similar study conducted in the Red River of the North Basin in Minnesota and North Dakota (Brigham and others, 1998).

In contrast to the results for the streambed sediment, lead generally was not detected in fish livers obtained from the study unit (fig. 5). The only detectable concentration of lead was in carp livers obtained from the Mississippi River at Minneapolis, Minnesota (site 12).

Mercury was detected in fish livers from 14 of the 25 sites sampled in the study unit (fig. 5). The greatest concentrations were measured in shorthead red-

Table 7. Fish species obtained in the study unit for analysis of trace elements in the Upper Mississippi River Basin study unit, 1995–96

[Map identifier corresponds to site listed in table 1; na, not available]

Map identifier	Site name	Drainage area (square miles)	Fish species (common name)	Average total length (inches)	Average weight (ounces)	Approximate age
1	Mississippi River at Grand Rapids, Minn.	3,320	White sucker	16.6	29.2	5 years
2	Mississippi River below Little Falls, Minn.	11,300	Shorthead redhorse	15.5	24.6	4 years
			Common carp	22.9	116.0	na
3	Sauk River at Richmond, Minn.	818	Common carp	25.5	115.0	9 years
4	North Fork Crow River above Paynesville, Minn.	232	Common carp	12.5	13.6	na
5	Crow River below State Highway 101 at Dayton, Minn.	2,770	Shorthead redhorse	19.6	49.3	7 years
6	Cedar Creek near Coopers Corner, Minn.	27.3	White sucker	11.2	9.1	na
7	Rum River at Anoka, Minn.	1,560	Common carp	18.1	45.3	6 years
8	Mississippi River near Anoka, Minn.	19,200	Common carp	18.2	48.6	7 years
9	Shingle Creek at Zane Ave. at Brooklyn Park, Minn.	19.2	White sucker	11.0	9.1	na
10	Shingle Creek at Queen Ave. in Minneapolis, Minn.	28.2	White sucker	9.0	4.6	na
			Common carp	6.7	2.7	na
11	Shingle Creek at 46th Street in Minneapolis, Minn.	40.8	White sucker	7.8	2.8	na
12	Mississippi River at 28th Ave. NE in Minneapolis, Minn.	19,600	Common carp	17.4	42.0	na
13	Little Cobb River near Beauford, Minn.	130	Common carp	19.6	58.3	na
14	Minnesota River near Jordan, Minn.	16,200	White sucker	17.9	46.3	6 years
15	Nine Mile Creek hear James Circle at Bloomington, Minn.	44.6	White sucker	11.8	11.0	3 years
16	Mississippi River at Nininger, Minn.	37,000	Common carp	17.6	43.7	4 years
17	Namekagon River at Leonards, Wisc.	128	White sucker	11.1	8.7	4 years
18	Namekagon River above Spring Lake Creek near Hayward, Wisc.	208	White sucker	8.3	3.7	na
19	St. Croix River near Danbury, Wisc.	1,510	Shorthead redhorse	15.9	22.9	6 years
			Golden redhorse	15.2	22.6	5 years
20	Kettle River near Kettle River, Minn.	5,510	White sucker	8.7	4.4	1 year
21	St. Croix River near Sunrise, Minn.	170	Shorthead redhorse	16.3	25.6	5 years
22	St. Croix River at Hudson, Wisc.	7,340	Common carp	18.7	50.5	6 years
23	Vermillion River near Empire, Minn.	129	White sucker	10.6	6.5	3 years
24	Cannon River at Lake Byllesby near Cannon Falls, Minn.	1,150	Common carp	17.7	44.2	6 years
26	Mississippi River at Lake Pepin at Central Point, Minn.	47,300	Common carp	na	53.0	6 years

Table 8. Summary statistics for trace elements in fish livers from individual species at all sites sampled in the Upper Mississippi River Basin study unit, 1995–96

[Concentrations are in micrograms per gram dry weight]

Constituent	Number of samples	Median	Coefficient of Variation	Minimum	Maximum
Aluminum	28	<1.00	0.996	<1.00	4.434
Antimony	28	all values less than reporting limits which ranged from 0.10 to 0.66 µg/g			
Arsenic	28	0.17	0.892	<0.20	0.70
Barium	28	<0.10	1.305	<0.10	0.70
Beryllium	28	all values less than reporting limits which ranged from 0.10 to 0.66 µg/g			
Boron	28	1.2	0.801	<0.2	3.6
Cadmium	28	0.50	0.898	<0.20	1.60
Chromium	28	0.60	0.977	<0.33	3.2
Cobalt	28	all values less than reporting limits which ranged from 0.10 to 0.66 µg/g			
Copper	28	51	0.613	17	170
Iron	28	355	0.920	120	2500
Lead	28	<0.25	0.512	<0.10	0.70
Manganese	28	6.90	0.441	2.8	16
Mercury	28	0.06	1.309	<0.01	0.70
Molybdenum	28	0.90	0.324	0.60	2.10
Nickel	28	<0.30	1.632	<0.10	0.80
Selenium	28	3.80	0.423	1.30	8.30
Silver	28	<0.20	0.991	<0.2	0.90
Strontium	28	0.2	0.8332	<0.1	1.1
Uranium	28	all values less than reporting limits which ranged from 0.10 to 0.66 µg/g			
Vanadium	28	0.40	0.863	<0.20	1.20
Zinc	28	180	0.988	59	1500

horse livers from the St. Croix River near Sunrise, Minnesota (site 21); and the Crow River below State Highway 101 at Dayton, Minnesota (site 5); and white sucker livers from the Vermillion River near Empire, Minnesota (site 23).

The sites with the greatest concentrations of mercury in fish livers (sites 1–5, 8, 13, 17, 19–21, and 23) were located outside of the TCMA (fig. 6). Mercury was not detected in fish livers from Shingle Creek at 46th Street in Minneapolis, Minnesota and the Mississippi River at 28th Ave. NE in Minneapolis, Minnesota (sites 11 and 12) even though the greatest concentrations of mercury in streambed sediment were measured at these locations. These results suggest that some environmental factor, possibly related to land use or geographic location, influences mercury partitioning between fish livers and streambed sediment. Mercury concentrations in fish livers may be related to the percent of the drainage area in wetlands (Zillioux and others, 1993). However, data collected as part of this study showed no correlation between fish liver mercury concentration and the percent of the land cover in wetlands (Kendall tau correlation coefficient = 0.148).

QUALITY ASSURANCE RESULTS

Quality assurance sampling, which included split replicate samples, indicated there was little variability in trace element concentrations in the streambed sediment due to sample processing, analysis, or collection procedures. The coefficient of variation was less than 5 percent for 77 percent of the constituents evaluated and less than 10 percent for 95 percent of the constituents evaluated. The constituents with the greatest coefficients of variation were arsenic (35 percent), mercury (9 percent), and thorium (13 percent). Differences among beryllium, bismuth, europium, gold, holmium, molybdenum, tantalum, and tin concentrations were not assessed due to data below the method reporting limit.

Assessment of the intra-site variability among streambed sediment collected from two different depositional zones in the Crow River (site 5) generally indicated no substantial differences between trace element concentrations. Thirty-nine constituents were evaluated in this analysis. Differences between antimony, bismuth, europium, gold, holmium, molybdenum, tantalum, and tin concentrations in the streambed sediment were not assessed because most of the concentrations for these constituents were below the method reporting limit. The coefficient of variation between concentrations measured in the streambed sediment collected near the right and left sides of the stream was less than five percent for 27 of the 39 constituents evaluated and less than 10 percent for 33 of the 39 constituents evaluated. The greatest coefficients of variation were for arsenic (12 percent), lead (11 percent), niobium (13 percent), silver (71 percent), sulfur (11 percent), and thorium (16 percent).

Quality-assurance sampling showed the variability in the concentrations of trace elements measured in fish livers generally was greater than those for stre-

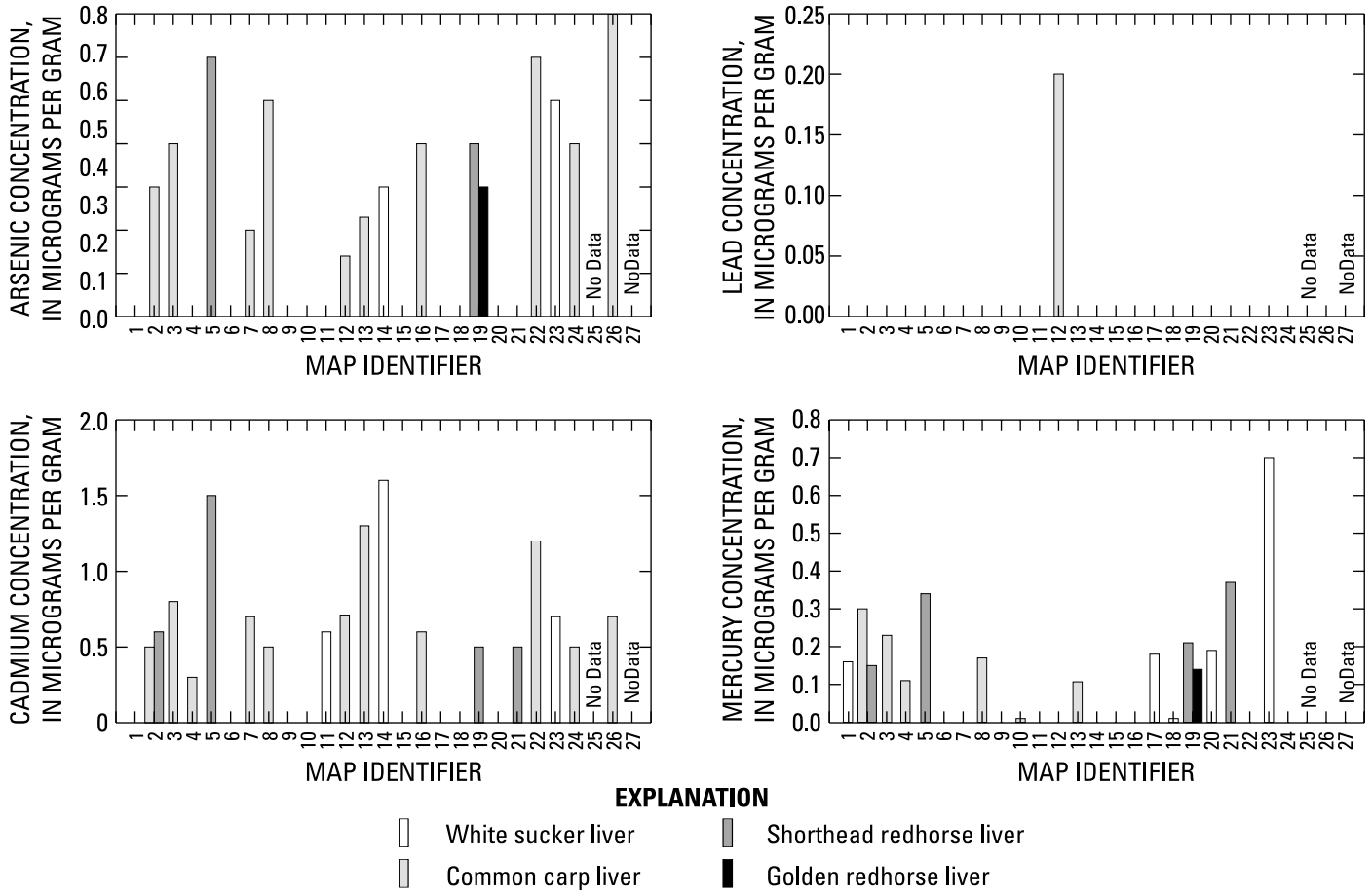

Figure 5.--Detected arsenic, cadmium, lead, and mercury concentrations in fish liver samples obtained from the Upper Mississippi River Basins study unit, 1995-1996 [Map identifier corresponds to sites in figures 2 and 3 and table1].

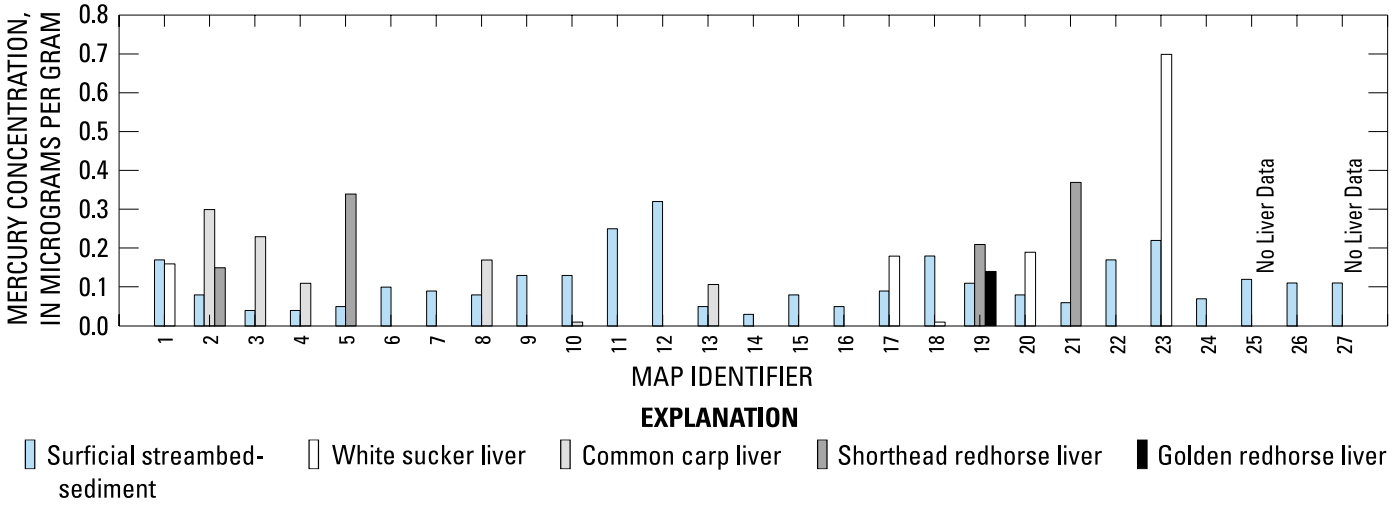

Figure 6.--Detected concentrations of mercury in streambed sediment and fish liver samples obtained from the Upper Mississippi River Basins study unit, 1995-1996 [Map identifier corresponds to sites in figures 2 and 3 and table1].

ambed sediment. The coefficient of variation was less than 10 percent for 8 percent of the constituents that could be evaluated and less than 25 percent for 75 percent of the constituents evaluated. The trace elements with the greatest coefficients of variation were boron (35 percent), strontium (61 percent), and selenium (77 percent). Aluminum, antimony, barium, beryllium, chromium, cobalt, lead, mercury, nickel, and uranium were not detected in the two replicate fish liver samples that were analyzed, so the variability in the concentrations of these constituents could not be assessed.

RELATION BETWEEN CONCENTRATIONS IN FISH LIVERS AND STREAMBED SEDIMENT

Correlations between trace element concentrations in fish livers and streambed sediment were virtually nonexistent to moderate (table 9). The strongest correlation was for barium. No correlations could be determined for antimony, beryllium, cobalt, molybdenum, and uranium concentrations because all concentrations measured in either the streambed sediment or fish livers were below the reporting limit.

IMPLICATIONS FOR WATER QUALITY AND AQUATIC BIOTA

This study indicated that elevated concentrations of some trace elements in streambed sediment in the UMIS study unit—in particular, antimony, cadmium, copper, lead, nickel and zinc—were strongly related to urban land use. These results were consistent with other studies that analyzed trace element concentrations in streambed sediment across the Nation (Novotny and others, 1993; Bevans and others, 1998; Frick and others, 1998; Peters and others, 1998; Wall and others, 1998; and Wentz and others, 1998) that determined elevated concentrations of some trace elements were related to urban land use. Sources of trace elements in urban areas include wastewater discharges, sanitary landfills, waste incineration, combustion of fossil fuels, batteries, and paints. Concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc measured in the streambed sediment from the study unit were similar to those measured for 20 other NAWQA study units that sampled streambed sediment during 1992 through 1995 (Rod Deweese, U.S. Geological Survey, oral commun., 1999). This indicates that concentrations of these elements measured in the streambed sediment of the UMIS study unit probably were not increased compared to other parts of the Nation. There are currently no state or Federal standards set for the amount of trace elements contained in streambed sediment.

Trace elements associated with streambed sediment have the potential to be released back into the water column under certain physical and chemical conditions, such as periods of extremely low dissolved oxygen concentrations or pH. Trace elements associated with streambed sediment also may be transported to downstream locations during high-flows.

There was no clear pattern in the distribution of trace elements in fish livers across the study unit. There generally were no relations between the concentration of trace elements measured in the streambed sediment and those measured in fish livers. Other researchers (Beauvais and others, 1995) have determined that elevated concentrations of cadmium in burrowing mayflies (*Hexagenia*) from the Mississippi River were coincident with elevated concentrations in the streambed sediment. These results indicate that some of the cadmium associated with streambed sediment in the study unit was bioavailable. Concentrations of mercury measured in fish livers from the study unit could not be related to those listed for fish consumption in the states of Minnesota and Wisconsin because the fish consumption advisories apply to mercury in fish fillets not livers.

Table 9. Kendall tau correlation coefficients of trace element concentrations in streambed sediment and fish livers in the Upper Mississippi River Basin study unit, 1995–96.

Trace element	Kendall tau correlation coefficient	Trace element	Kendall tau correlation coefficient	Trace element	Kendall tau correlation coefficient
Aluminum	-0.143	Cobalt	Not available	Nickel	0.104
Antimony	Not available	Copper	0.171	Selenium	0.145
Arsenic	-0.037	Iron	0.077	Silver	0.199
Barium	-0.582	Lead	0.131	Strontium	-0.113
Beryllium	Not available	Manganese	0.092	Uranium	Not available
Cadmium	-0.268	Mercury	-0.174	Vanadium	0.011
Chromium	0.066	Molybdenum	Not available	Zinc	0.137

SUMMARY

Trace elements were analyzed in streambed sediment and fish livers in part of the Upper Mississippi River Basin to describe their occurrence and distribution, describe relations of the concentrations measured to natural and anthropogenic factors, and describe any relation between concentrations in streambed sediment and fish livers as part of the U.S. Geological Survey's National Water-Quality Assessment Program. The study unit included the part of the Upper Mississippi River from its source in northern Minnesota to the outlet of Lake Pepin, a natural lake on the river located near Red Wing, Minnesota. Sampling was conducted from 1995 through 1996. Streambed sediment were collected from 27 sites, and fish were obtained from 25 sites. Sampling sites were selected to characterize the occurrence and distribution of trace elements across the study unit and assess the major natural and anthropogenic factors expected to affect concentrations (glacial deposit composition, texture of surficial glacial deposits, and general land use and land cover).

All of the trace elements analyzed in streambed sediment were detected except bismuth, europium, gold, holmium, molybdenum, tantalum, and tin. The elements with the greatest variability among the sites were antimony, arsenic, cadmium, copper, lead, manganese, mercury, niobium, silver, sulfur, and zinc.

The occurrence and distribution of trace elements in streambed sediment from the study unit were related to the composition of surficial glacial deposits covering the study unit and land use. Streambed sediment derived from calcareous surficial glacial deposits were associated with the elements aluminum, barium, beryllium, calcium, cerium, gallium, lanthanum, lithium, magnesium, neodymium, potassium, and strontium. Streambed sediment strongly influenced by the siliceous glacial deposits from the Superior or Rainy Lobes of the Laurentide Ice Sheet were associated with the elements chromium, copper, nickel, scandium, titanium, vanadium, ytterbium, and yttrium.

Concentrations of antimony, arsenic, cadmium, copper, lead, mercury, nickel and zinc in the streambed sediment were primarily related to urban land use. Elevated concentrations of these elements generally occurred at sites located within or near urban areas in the study unit. The greatest concentrations of most of these elements generally occurred in streambed sediment obtained from Shingle Creek. Lead concentrations in sediment from Shingle Creek increased in the downstream direction. The greatest lead concentrations in Shingle Creek were measured in sediments obtained from the most downstream site, which was located in Minneapolis, Minnesota. This pattern of lead concentrations probably reflects the past use of leaded gasoline, pesticides, or paints.

Cadmium concentrations in streambed sediment collected from the Mississippi River were greatest at Nininger, Minnesota and Lake Pepin. This indicates inputs of cadmium into the Mississippi River from the Twin Cities metropolitan area. Lead concentrations in Lake Pepin were greatest in the sediment collected from the site located near Frontenac, Minnesota, which probably reflects the settling out of particulate matter in the upstream part of the lake.

Arsenic concentrations were greatest in streambed sediment collected from Cedar Creek near Coopers Corner, Minnesota; Shingle Creek; and the Vermillion River near Empire, Minnesota. Increased arsenic concentrations in sediments from Cedar Creek near Coopers Corner, Minnesota; the Vermillion River near Empire, Minnesota; and Shingle Creek at Zane Avenue in Brooklyn Park, Minnesota may have been a result of a local source of sulfide minerals or the preferential sorption of arsenic to the streambed sediment because the iron content in the sediment from these sites was greater relative to most of the other sites sampled in the study unit. The greatest concentrations of mercury were measured in streambed sediment from the Mississippi River at Grand Rapids and Minneapolis, Minnesota; Shingle Creek at 46th Street in Minneapolis, Minnesota; the Namekagon River above Spring Lake Creek near Hayward, Wisconsin; the St. Croix River at Hudson, Wisconsin; and the Vermillion River near Empire, Minnesota.

All of the trace elements analyzed were detected in fish livers except antimony, beryllium, cobalt, and uranium. Concentrations of elements, which are essential for metabolism, generally were greater than the other constituents analyzed. Ranges for concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc were similar to those measured in 20 other NAWQA studies across the United States from 1992 through 1995. Cadmium concentrations in fish livers were moderately correlated to fish length and weight. There was no relation between trace element concentrations in fish livers and streambed sediment in the study unit.

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